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Published in:
Marine Chemistry

DOI:
10.1016/S0304-4203(97)00067-4

Publication date:
1997

ELSEVIER

Marine Chemistry 59 (1997) 87–93

MARINE CHEMISTRY

The global Cd/phosphate relationship in deep ocean waters and the need for accuracy

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Received 9 October 1996; revised 7 May 1997; accepted 23 May 1997

Abstract

The relationship between Cd and phosphate is intriguing for unravelling geochemical cycling in the modern ocean. Moreover it is relevant for reconstructing Cd or phosphate distributions in paleoceanography. Whether the global Cd/phosphate data indicate a single linear relationship or whether the data are better described by two different linear relationships, one for the North Atlantic Ocean data and one for the Indo–Pacific Ocean data, is still a matter of debate. Recently, new data have become available for the Southern hemisphere which partly fill a gap that existed between the North Atlantic and Indo–Pacific Ocean data. The model with two different relationships for the North Atlantic and the Indo–Pacific Ocean deviated with statistical significance from a single global linear relationship. Yet, both models are characterized by a large residual variance likely due to apparent differences in accuracy between different laboratories. If these laboratory effects are taken into account in the models, the difference between the relationships of the North Atlantic and the Indo–Pacific Ocean remains statistically significant. However, when only two data sets with the smallest phosphate concentrations ($PO_4 < 1$ μM) are left out the significance disappears. However, it is still risky to be too conclusive on basis of the present data. More accurate Cd- and phosphate-data are needed, especially in the low concentration area. Accuracy become be improved by the availability and use of international reference standards in combination with regular spike-recovery experiments. © 1997 Elsevier Science B.V.

Keywords: trace metals; cadmium; review; theoretical; statistics

1. Introduction

Two decades ago Boyle et al. (1976) and Martin et al. (1976) as well as Bruland et al. (1978); Bruland (1980); Knauer and Martin (1981) demonstrated that Cd is very closely correlated with phosphate. This led Hester and Boyle (1982) to suggest a linear relationship with zero intercept between the global Cd- and phosphate- data. Soon afterwards Bruland and Franks (1983) found a Cd–phosphate slope for the North Atlantic Ocean, which was 15% lower than the slope for the North Pacific Ocean. Boyle (1988) combined a selection of 8 out of 16 available Cd–phosphate data sets in one Cd–phosphate plot and suggested a uniform global Cd–phosphate relationship consisting of two separate Cd/phosphate relations, one for phosphate concentrations lower than 1.3 μM and one for phosphate concentrations higher than 1.3 μM. However, the selection criterion

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PII S0304-4203(97)00067-4

for quality of data was not reported, whereas among the 8 selected sets one preliminary data set eventually was not published and two others were from a shallow inshore site off Gibraltar (Boyle et al., 1985) and the semi-enclosed Gulf of Mexico (Boyle et al., 1984). Here exchange processes of Cd and phosphate with the continental shelf may have obscured the oceanic trend.

More recently Frew and Hunter (1992, 1995), De Baar et al. (1994), Frew (1995) and Yeats et al. (1995) provided evidence in support of apparently two Cd/phosphate relationships. Frew and Hunter (1992, 1995) suggested that the low Cd/phosphate relationship in the subantarctic region of the Pacific Basin plays a major role in the formation of these two relationships. Two mechanisms were suggested: (I) ventilation of low Cd/phosphate subantarctic water to intermediate depth by formation of Antarctic Intermediate Water (AAIW), (II) remineralization of low Cd/phosphate detritus from biota produced in waters formed at the subtropical convergence. However, their subantarctic data do not represent the AAIW source area (Saager, 1994, p. 107). Frew (1995) provided another hypothesis attributing the apparent global Cd/phosphate kink to the formation of Antarctic Bottom Water (AABW), which has as a major component near-surface waters, which presumably would have a high Cd/phosphate ratio.

De Baar et al. (1994) proposed a selection criterion for high quality Cd and phosphate data as Cd/phosphate ratios below 1000 m having a coefficient of variation less than 10%. This ensures that selected data are of reasonable precision, without suggesting that non-selected data are of lesser quality. However, independent assessment of the accuracy of the data is still lacking. Using the selection criterion mentioned above, De Baar et al. (1994) obtained a selected data set for deep waters showing two data clusters with different Cd/phosphate slopes between North Atlantic data, and Pacific/Indian/Antarctic Ocean data. When ignoring the gap between clusters one global relationship was found (De Baar et al., 1994). The need for more data filling the gap in deep waters of the temperate Southern hemisphere was recognized for validating the hypothesis of a single uniform global Cd/phosphate relationship. Recently new data have become available for the Southern hemisphere.

The new data are added in the present paper using the same selection criterion as De Baar et al. (1994). For some stations the water column was divided in different water masses, because hydrography is a very important factor in the circulation of trace metals and nutrients. For each water column the selection criterion was used separately.

The methodology of the present paper differs in two important aspects from that of De Baar et al. (1994): whereas De Baar et al. (1994) used all selected data below 1000 m depth as separate data points, the present paper used for each sample site the average Cd and phosphate concentration because the accuracy of data of one sample site are not independent from each other. Besides that, the possible laboratory bias was taken into consideration directly in the model formulation.

2. Methods

By the use of the same selection criterion as De Baar et al. (1994), data by Yeats (1988), Hunter and Ho (1991), Westerlund and Öhman (1991), Frew and Hunter (1992), Martin et al. (1993), De Jong et al. (1994), Pai and Chen (1994), Frew (1995), Yeats et al. (1995) and Löscher et al. (submitted) are added to the selected data by De Baar et al. (1994). The added data are presented in Table 1.

One station by Westerlund and Öhman (1991) for the Weddell Sea was added. The site appears far enough away from the continental shelf to assume that processes occurring in the shelf would be of no importance. The same goes for the data by Pai and Chen (1994), where only the two offshore stations far enough from the continental shelf were added.

De Baar et al. (1994) omitted the data by Hunter and Ho (1991) because the concentrations of Cd and phosphate increase regularly with depth. Latter data are used in the current selection, because they otherwise fall within the selection criterion for the Cd/PO_4 ratio. The data by Frew and Hunter (1992) were added as well.

In waters like the Southern Ocean the circulation of different water masses is an important factor in controlling the metal and nutrient concentrations. For this reason at four stations by Löscher et al., submitted the water column was divided into different water masses in case the coefficient of variation of

the Cd/phosphate ratio varied more than 10% in the water column below 1000 m. The same was done for the Southeast Atlantic data set of Yeats et al. (1995). Then for each water mass the selection criterion was applied separately as reported in Table 1.

3. Results and discussion

Fig. 1a shows Cd versus phosphate concentrations of the new deep water data (Table 1) superimposed on the selected data set by De Baar et al. (1994). The

Table 1
Cd–phosphate data added to the selected stations by De Baar et al. (1994). For the added data the same selection criterion is used. For stations where the coefficient of variation of the Cd/phosphate ratio is not lower than 10% over the whole water column deeper than 1000 m, the water column was divided into the different water masses. For each water mass the selection criterion was applied separately

Latitude/ longitude	Refs.	n	Depth (m)	Cd (pM)	CV_{Cd} (pM)	PO_4 (μM)	$CFUNCCV_{FUNCPO_4}$ (μM)	Cd/PO_4 (pM/μM)	$CV_{Cd/P}$ (pM/μM)	%
64°S; 47°W	Westerlund and Öhman (1991)	7	1000–3000	683	59	2.49	0.06	274	20	7
38°S; 167°E	Hunter and Ho (1991)	3	1000–1500	523	38	1.83	0.21	287	20	7
36°S; 163°E	Hunter and Ho (1991)	5	1083–1793	650	81	2.16	0.16	300	29	10
35°S; 167°E	Hunter and Ho (1991)	4	1083–1723	662	83	2.23	0.16	296	18	6
35°S; 170°E	Hunter and Ho (1991)	3	1144–1621	657	15	2.25	0.14	292	21	7
35°S; 171°E	Hunter and Ho (1991)	5	1096–1494	712	77	2.39	0.12	297	18	6
48°S; 164°E	Frew and Hunter (1992) [a]	19	1000–4450	595	58	2.34	0.12	254	16	6
62°S; 83°E	Frew (1995)	3	1259–2440	615	8	2.19	0.08	281	8	3
65°S; 84°E	Frew (1995)	5	1275–3089	686	28	2.28	0.01	300	12	4
15°S; 0°E	Yeats et al. (1995)	4 [b]	1351–2201	414	73	1.66	0.19	249	15	6
30°S; 8°E	Yeats et al. (1995)	4 [c]	1081–1481	695	52	2.15	0.09	324	21	6
		4 [c]	2551–3410	403	33	1.60	0.05	252	23	9
		4 [c]	3710–4830	599	52	1.84	0.15	326	16	5
46°S; 1°E	Löscher et al. (submitted)	4 [d]	1234–1976	619	57	2.11	0.11	293	29	10
		8 [d]	2953–4149	649	52	2.26	0.08	287	23	8
52°S; 6°W	Löscher et al. (submitted)	7	987–2117	735	39	2.26	0.05	326	14	4
54°S; 6°W	Löscher et al. (submitted)	9	988–2562	746	37	2.32	0.04	318	17	5
56°S; 12°W	Löscher et al. (submitted)	2 [e]	4509–4744	808	13	2.29	0.06	345	3	1
58°S; 6°W	Löscher et al. (submitted)	5 [f]	2460–3675	692	63	2.28	0.04	303	30	10
34°N; 13°W	Yeats et al. (1995)	22	1000–4377	267	61	1.24	0.19	215	20	9
35°N; 62°W	Yeats (1988)	7	1200–4675	304	26	1.23	0.06	247	14	6
47°N; 20°W	Martin et al. (1993)	5	1100–2900	257	31	1.15	0.07	188	10	5
59°N; 20°W	Martin et al. (1993)	6	1000–2800	210	10	1.23	0.05	170	7	4
55°N; 49°W	De Jong et al. (1994)	13	1200–3682	253	19	1.04	0.05	244	26	10
52°N; 34°W	De Jong et al. (1994)	10	1000–3520	267	20	1.08	0.04	247	18	7
65°N; 31°W	De Jong et al. (1994)	6	1078–1374	256	33	0.94	0.10	273	28	10
22°N; 124°E	Pai and Chen (1994)	6	1002–4294	997	41	2.68	0.17	372	12	3
22°N; 127°E	Pai and Chen (1994)	7	1003–5000	1003	31	2.69	0.18	374	18	5

[a] The data by Frew and Hunter (1992) are added too because Frew and Hunter (1995) recently demonstrated the accuracy of their phosphate data. De Baar et al. (1994) omitted these stations because of a consistent difference between Frew and Hunter (1992) phosphate data and those of the nearby GEOSECS station 280, a discrepancy which at the time could not be resolved by the authors.

[b] The water column of station 7 is divided after Measures et al. (1995); into three different water masses: 1351–2201 m: North Atlantic Deep Water (NADW), 2353–3604 m: linear mixing with lower NADW of the western boundary undercurrent and 4604–4804 m: mixing towards Antarctic Bottom Water (AABW). Only the NADW falls within the selection criterion.

[c] The water column of station 9 is divided after Measures et al. (1995); into four different water masses: 1081–1481 m: Upper Circumpolar Deep Water (UCDW), 1801–2401 m: Labrador Sea Water (LSW), 2551–3410 m: NADW-complex and 3710–4830 m: AABW. The LSW does not fall within the selection criterion.

[d] 1234–1976 m: UCDW 2953–4149 m: Lower Circumpolar Deep Water (LCDW).

[e] 988–2562 m: LCDW.

[f] 2460–3502 m: AABW.

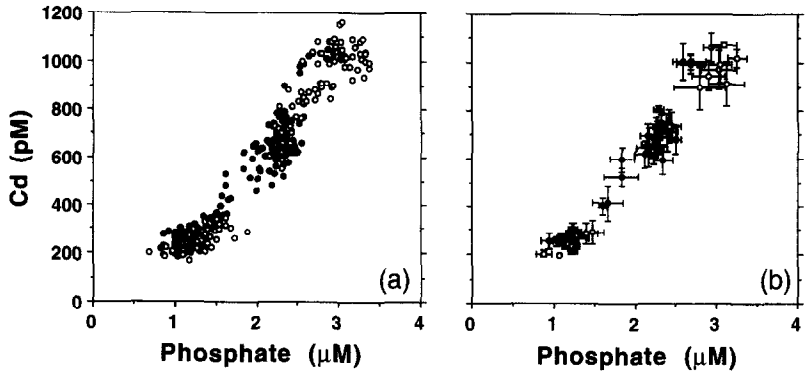

Fig. 1. Global Cd/phosphate data for water depths > 1000 m. Open circles indicate selected data after De Baar et al. (1994). The filled circles show added data (Table 1). (a) Individual data points. (b) Average data at each selected station with standard deviations.

gap of the Cd–phosphate data between the deep Atlantic Ocean and the deep Antarctic/Pacific/Indian Ocean is now filled with new data, although there still are only a few data with phosphate concentrations between 1.8 and 2.0 μM. Apparently, the errors are not independent. For example, all data in the range of phosphate concentration between 1.2 and 1.7 μM fall below, and all data with a phosphate concentration < 1.0 μM fall above the overall regression line. This dependence, however, is not surprising as at each sample site multiple samples are taken at different depths. The errors from the overall regression line most likely are correlated between such samples from the same location. This dependence may, for example, be due to laboratory bias since the samples at one station in general have been

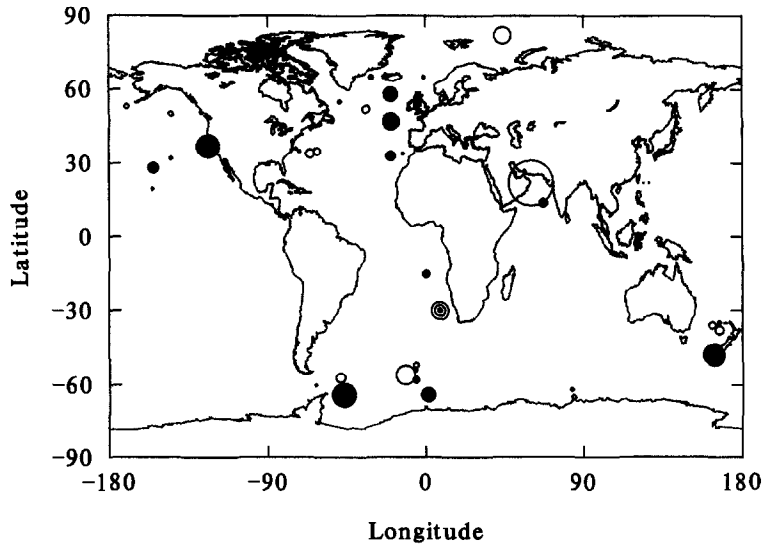

Fig. 2. The deviations of the Cd concentrations of the selected stations from the prescribed global uniform linear Cd/phosphate relationship, after initial correction of the Cd data for the Cd-deviation through different accuracy of the laboratory groups from the global uniform relationship. The size of the circles indicates the magnitude of the Cd concentration deviation from the assumed global uniform linear Cd/phosphate relationship. The open circles stand for a positive residual deviation and the filled circles for a negative residual deviation.

analyzed simultaneously. Therefore the average Cd and phosphate data from the selected stations were used (data by De Baar et al., 1994; with added data, Table 1) for further analyses. They were plotted together with their standard deviation in Fig. 2. As various laboratories worked at more than one site, dependence between the data may not have been removed completely. Therefore, a laboratory (-group) effect was included in the model. Thus, when assessing the general linear relationships:

$$[\mathrm{Cd}] = a + b[\mathrm{PO_4}] \quad (1)$$

the following model was fitted and the contribution of the various factors was tested.:

$$[\mathrm{Cd}] = a + A_i + (b + B_i)[\mathrm{PO_4}] + C_j + \varepsilon \quad (2)$$

where a is the overall constant; A_i the deviation of the overall constant for area i; b is the overall slope; B_i is the deviation of the overall slope for area i; C_j is the laboratory group effect for group j; ε is the residual error, and where $i = 1$ for the North Atlantic Ocean data ($PO_4 < 1.5$ μM) and $i = 2$ for the other ocean data ($PO_4 > 1.5$ μM); $j = 1, \ldots, K$, where K is the number of laboratory groups.

Table 3 gives an overview about the references which belong to one laboratory group.

Constraints on the parameters are

$\Sigma A_i = 0$, so $A_1 = -A_2$,

$\Sigma B_i = 0$, so $B_1 = -B_2$,

$\Sigma C_j = 0$.

Both, the group effect and the ocean effect (which accounts for a different intercept and slope for the North Atlantic data compared to the other oceans) were significant (Table 2). That means that the existing data set still conforms to different Cd/phosphate relationships for the Atlantic and the Indo–Pacific Ocean when different accuracies of the laboratory groups are assumed. One may wonder whether there are deviations of the overall model on finer spatial scale. Fig. 2 shows the residuals of the single Cd/phosphate relationship including a correction for laboratory group effects. The world-wide distribution of the residuals gives no indication for a specific ocean area with a constant deviating Cd-phosphate character.

However, leaving out the two smallest average phosphate concentrations ($PO_4 < 1$ μM) and fitting the models again, the single Cd/phosphate relationship was not statistically significant deviating from the two lines model. According to the parsimony principle (Ockham's razor) which contents that the simplest model is the best description of reality, the

Table 2
F test for the various factors of the fitted model (Eq. (2)), whereby df: degree of freedom; SS: sum of squares and; MS: mean square

Factors	df	SS	MS	F	P
PO_4	1	33701	33701	13.3	0.001
A_i & B_i	2	18149	9074	3.3	0.048
Group	10	75069	7507	2.73	0.013
Error	36	99000	2750		

Table 3
Classification of laboratories into 11 groups (separated by lines) as applied in the statistical models, i.e. Eq. (2). Given the similar performance the data from UCSC (Bruland and co workers) and MLML (Martin and co workers) were grouped together for sake of convenience

Danielsson and Westerlund (1983)
Danielsson et al. (1985)
Sakamoto-Arnold et al. (1987)
Bruland et al. (1978)
Bruland (1980)
Bruland and Franks (1983)
Knauer and Martin (1981)
Martin et al. (1985)
Martin et al. (1989)
Martin et al. (1990)
Martin et al. (1993)
Nolting (JGOFS, 27 April 1990)
Nolting et al. (1991)
Saager (JGOFS, 4 June 1990)
Saager (JGOFS, 10 June 1990)
Saager et al. (1992)
Boyle et al. (1976)
Frew and Hunter (1992)
Frew (1995)
Hunter and Ho (1991)
Westerlund and Öhman (1991)
Yeats (1988)
Yeats et al. (1995
Löscher et al. (submitted)
De Jong et al. (1994)
Pai and Chen (1994)

Table 4
Deviation in Cd concentrations of the different laboratory groups from the single linear Cd/phosphate relationship. The sequence of the groups in this table has no correlation with the sequence in Table 3

Group	Laboratory effect (Cd [pM])
1	−60
2	−50
3	−36
4	−28
5	−26
6	−22
7	−6
8	−4
9	16
10	94
11	121

single regression line should be used. Yet, we believe that, given all uncertainties about the independence of errors, at the moment it is still too early to make conclusions. More accurate data are needed especially from the Northern hemisphere with low phosphate concentrations ($PO_4 < 1$ μM).

Table 4 shows the deviation of the Cd concentration of the different laboratories from the linear relationship. The deviation lays between −60 and 121 pM, similar to that found in a recent intercalibration study (fig. 3 of Yeats et al., 1995). In order to improve the accuracy the use of certified standards is needed, both for Cd and phosphate. Briefly, the internal precision of a laboratory is often quite satisfactory for phosphate and Cd, but accuracy is lacking. For phosphate Saager (1994, pp. 40–41) found discrepancies of various data set when compared with nearby GEOSECS stations. Similarly, the GEOSECS data set of phosphate and nitrate in the Southern Ocean (> 30°S) has a much more tight correlation than the corresponding NODC (National Oceanographic Data Center) database assimilated from various field programs and laboratories (Kamykowski and Zentara, 1989). The preparation and stability of nutrients standards (Aminot and Kérouel, 1996) is therefore a matter of great urgency. Similarly, there is a need for production and routine use of certified standards of Cd and other metals. Finally, for Cd and other metals the APDC/DDDC extraction method has less perfect recovery than commonly assumed (Muller et al., 1991).

Acknowledgements

This research was supported by grants from the *Commissie Antarctisch Onderzoek* and the *Nederlandse Organisatie voor Wetenschappelijk Onderzoek* (NWO) and the graduate student fellowship from NWO/GOA to the first author. This is NIOZ contribution number 3183.

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